FORM PTO-1390
(REV 12-29-99)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER
VER-137XX

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 36 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
09/720068

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/NL99/00389	24 June 1999	25 June 1998

TITLE OF INVENTION PROCESS FOR REGENERATING A USED PRECIOUS METAL CATALYST

APPLICANT(S) FOR DO/EO/US MariusVaarkamp

Applicant herewith submits to the United states Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT WITH AMENDED CLAIM 1

Express Mail Number
EL418428851US

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/720068	PCT/NL99/00389	VER-137XX

17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

		CALCULATIONS PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	**$1,000.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	**$860.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$710.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$690.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	**$100.00**	

ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	18 - 20 =	0	X **$18.00**	$ 0	
Independent claims	1 - 3 =	0	X **$80.00**	$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+**$270.00**	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				$	
SUBTOTAL =				$ 860.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$	
TOTAL NATIONAL FEE =				**$ 860.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property				$	
TOTAL FEES ENCLOSED =				$ 860.00	
				Amount to be refunded:	$
				charged:	$

a. ☒ A check in the amount of $ 860.00 to cover the above fees is enclosed. A check in the amount of $_____ is enclosed for the assignment recordation fee.

b. ☐ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0804 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Customer Number 207

SEND ALL CORRESPONDENCE TO:

Weingarten, Schurgin, Gagnebin & Hayes LLP
Ten Post Office Square
Boston, Massachusetts 02109

Date: 12-20-00

SIGNATURE

Charles L. Gagnebin III
NAME

25,467
REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application	:	Marius Vaarkamp
Application No.	:	
Filed	:	Herewith
For	:	PROCESS FOR REGENERATING A USED PRECIOUS METAL CATALYST
Examiner	:	
Attorney's Docket	:	VER-137XX

Group Art Unit:

* *

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231 on _____.

By: _____

Registration No.
Attorney for Applicant(s)

* *

PRELIMINARY AMENDMENT

BOX PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly enter the following Preliminary Amendment in the above-identified application:

In the Claims:

Please amend the Claims as follows:

Claim 1, line 4, after "acid" insert --in liquid state--;

Claim 3, line 1, delete "or 2";

Express Mail Number
EL484288815US

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Claim 4, line 1, delete "claims 1-3" and insert --claim 1--;

Claim 5, line 1, delete "claims 1-4" and insert --claim 1--;

Claim 6, line 1, delete "claims 1-5" and insert --claim 1--;

Claim 7, line 1, delete "claims 1-6" and insert --claim 1--;

Claim 8, line 1, delete "claims 1-7" and insert --claim 1--;

Claim 9, line 1, delete "claims 1-8" and insert --claim 1--;

Claim 10, line 1, delete "claims 1-9" and insert --claim 1--;

Claim 11, line 1, delete "claims 1-10" and insert --claim 1--;

Claim 12, line 1, delete "claims 1-11" and insert --claim 1--;

Claim 13, line 1, delete "claims 1-12" and insert --claim 1--;

Claim 14, line 1, delete "claims 1-13" and insert --claim 1--;

Claim 15, line 1, delete "claims 1-14" and insert

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--claim 1--; and

Claim 16, line 4, delete "claims 1-15" and insert --claim 1--.

Please add the following new claim 17:

17. Process according to claim 2, wherein:

the degree of dispersion is increased after the regeneration;

the acid impregnated catalyst is reduced in a flow of hydrogen gas;

the acid impregnated catalyst is oxidised in a flow of dry (<0.1 vol.% of water) air, followed by reduction;

the reduction and or oxidising step are carried out at a temperature of between 250 and 600°C;

the silica-alumina support has been prepared using a sol-gel method;

the support has an Si-Al atomic ratio of from 0.1 to 300;

the catalyst has a precious metal content of from 0.01 to 5 wt.%, calculated on the basis of the weight of reduced catalyst;

the catalyst is impregnated with an aqueous solution of the acid;

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the acid is selected from the group of HCl, H_3PO_4, H_2SO_4 HNO_3, HBr and combinations thereof;

the amount of acid calculated on the basis of a ratio of equivalents of acid to atoms of precious metal is between 0.1 and 100, preferably between 0.5 and 10;

prior to the impregnation, carbonaceous deposits on the catalyst are burned off;

the regeneration is carried out in a reactor, separate from the reactor in which the catalyst is used; and

the catalyst is a used catalyst from a process in the group consisting of hydrogenation, hydro-isomerisation, hydro-desulfurisation, hydrodewaxing and catalytic reforming.

18. Process for hydrogenation, hydro-isomerisation, hydro-desulfurisation or hydrodewaxing, comprising treating the feedstock in the presence of a catalyst that has been regenerated using the process of claim 17.

REMARKS

This Preliminary Amendment puts the claims into proper form for examination. Kindly calculate the filing fee based on the amended claims.

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The Examiner is encouraged to telephone the undersigned attorney to discuss any matter which would expedite allowance of the present application.

Respectfully submitted,

Marius Vaarkamp

By: _____
Charles L. Gagnebin III
Registration No. 25,467
Attorney for Applicants

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Dated: 12-20-00

CLG:mes/240226-1

09/720068
PCT/NL99/00389
JC01 Rec'd PCT/PTO 20 DEC 2000

Title: Process for regenerating a used precious metal catalyst

The present invention is directed to a process for regenerating a used precious metal catalyst by redispersing the precious metal. Regeneration of used precious metal catalysts is an important aspect of this type of catalyst technology, intended to extend the lifetime of the precious metal catalyst. Regeneration is generally performed in three steps, namely 1) Removal of carbonaceous deposits (usually by burning), 2) redispersion of the precious metal, and 3) reduction of the redispersed precious metal.

Various methods for regeneration of used precious metal catalyst by redispersion of the precious metal on the support are known. Generally the redispersion is done by treatment with oxygen, Cl_2 or Br_2.

In a review article of J.B. Butt and E.E. Petersen in Activation, Deactivation and Poisoning of Catalyst, Academic Press (1988), pp 214 to 232, it has been indicated that the following general types of redispersion procedures have been suggested: 1) thermal treatment in an oxygen atmosphere, 2) thermal treatment in oxygen followed by reduction in hydrogen, 3) high temperature treatment followed by rapid cooling or 4) chemical dissolution of contaminants and redispersion of the metal. In this article it has been indicated that the behaviour of a catalyst in redispersion experiments is very much dependent on the nature of the support. A platinum on alumina catalyst can for example be redispersed using air, whereas platinum on silica behaves totally different.

In WO-A 95/23643 a process has been described for the catalytic treatment of waste water, using a precious metal catalyst, which process includes as part of the overall process the regenerating of the catalyst. The regeneration of the catalyst which is a palladium on silica/carbon, is done

by washing with an organic solvent, and/or acid and/or by thermal treatment.

In US-A 3,804,777 a process has been described, wherein lead contaminants present in a precious metal catalyst are dissolved by percolating a dilute acid at ambient temperature through the catalyst, followed by treatment with hydrogen at about 100°C.

The present invention deals with a process for regenerating a precious metal catalyst on an amorphous silica alumina support. The inventors of the present invention have found that the conventional methods, for example such as reported by Butt et al, but also the methods using chlorine or bromine do not result in an increase of dispersion, as will be shown in the examples to be reported herein. Various known methods result in a decrease of the degree of dispersion.

It is an object of the present invention to provide a method for redispersing the precious metal present in a catalyst based on an amorphous silica-alumina support.

The process according to the present invention for the regeneration of a catalyst, said catalyst comprising at least one precious metal on an amorphous silica alumina support, comprises impregnating the catalyst with an acid, followed by reduction or oxidation of the impregnated catalyst at a temperature above 200°C.

The regeneration of the catalyst, as used herein, indicates a redispersion of the said at least one precious metal over the surface of the support.

Surprisingly it has been found that the use of an acid in a liquid state, such as an aqueous solution, followed by the specific thermal treatment results in a redispersion of the precious metal on the support, whereas other methods result in a decrease of the degree of dispersion.

Suitable precious metals for use in the catalyst to be regenerated by the process according to the present invention are platinum, palladium, gold, iridium, rhenium,

ruthenium, rhodium, osmium and silver. Also combinations of two or more of those precious metals can be used. So it is possible to use a combination of at least one of those precious metals with one or more other metals. The preferred catalyst to be regenerated by the process of the present invention is based on platinum and/or palladium.

The precious metal catalysts to be regenerated by the process of the present invention have generally been used for reactions involving hydrogenation, such as hydrogenation itself, hydro-isomerisation, hydro-desulfurisation and hydro-dewaxing. The may also have been used in dehydrogenation reactions, such as catalytic reforming. Once the performance of the catalyst decreases below a certain level the catalyst is regenerated. In some processes it is also usual to perform regeneration simply after a certain amount of time has passed, without waiting for a decrease of the activity.

The catalyst to be regenerated is, either in the reactor or in a separate plant, prepared for the actual redispersion experiment. This step includes the removal of carbonaceous deposits and other unwanted material on the catalyst. This can for example be done by washing using a suitable solvent and/or by burning of the contaminants.

Subsequently the catalyst is impregnated with an acid, preferably in an aqueous solution. Suitable acids are the usual mineral acids, including HCl, H_3PO_4, H_2SO_4, HNO_3, HBr, or combinations of two or more of these acids. The amount of acid on the basis of the ratio of equivalents of acid to atoms of precious metal is between 0.1 and 100, preferably between 0.5 and 10. After impregnating the catalyst with the acid, the impregnated catalyst is either reduced in a flow of hydrogen gas or oxidised in a flow of dry air, followed by reduction. In a more preferred embodiment both reduction and oxidation are carried out at a temperature of at least 250°C and more in particular between 250°C and 600°C.

After the final reduction step a supported catalyst is obtained usually having approximately the same degree of dispersion as the original catalyst. Sometimes the treatment even results in an increase of degree of dispersion. It is to be noted in this respect that the degree of dispersion is related to the precious metal crystallite size. The degree of dispersion can for example be determined by CO-chemisorption, whereby the amount of CO absorbed by the precious metal gives an indication of the number of metal atoms available on the surface of the metal crystallites. A larger amount of chemisorbed CO indicates a higher degree of dispersion, i.e. a smaller metal crystallite size.

An important aspect of the present invention resides therein that the catalyst to be regenerated is based on an amorphous silica alumina support. On the support a precious metal is present preferably in an amount of from 0.001 to 5 wt.%, calculated on the weight of the catalyst (in reduced form). The amorphous silica-alumina support is preferably prepared using a sol-gel method, whereas the support has an Si/Al atomic ratio of between 0.1 and 300. As has been indicated before, the type of support is extremely important in the selection of the regeneration method.

The present invention is now elucidated on the basis of a number of experiments.

EXAMPLES

In the examples the effect of various treatments on the dispersion of 0.7 wt.% platinum on a silica-alumina support having an Si/Al atomic ratio of 8 is shown. The catalyst support is prepared by a sol-gel method as for example described in International patent application PCT/NL98/00090. The fresh catalyst had an CO/Pt ratio of 0.25, which is a measure for the degree of dispersion of the precious metal.

Samples of this catalyst were subjected to various treatments, which are described in the subsequent table, together with the result thereof.

Table 1 Redispersion experiments for Pt/silica-alumina

treatment	CO/Pt
none	0.25
air 400°C	0.25
air 500°C	0.23
500°C, 0.8% Cl, 5% H2O, 2h	0.12
530°C, 0.8% Cl, 5% H2O, 4h	0.07
530°C, 0.8% Cl, 5% H2O, 2h	0.07
HCl imp, dry air 400°C	0.31
HCl imp, H2 300°C	0.33
HCl imp, wet air 400°C	0.07
HCl imp, wet HCl 200°C	0.12

As can be seen from this table, treatment with air had almost no influence, whereas treatment with a gas flow containing chlorine and water strongly decreased the dispersion. Also impregnating with hydrochloric acid, followed by wet air or wet hydrochloride at increased temperature resulted in a strong decrease of degree of dispersion. Only acid impregnation followed by treatment with dry air and hydrogenation, or acid impregnation followed by hydrogenation only, showed an improvement in the degree of dispersion.

Claims

1. Process for the regeneration of a catalyst, said catalyst comprising at least one precious metal on an amorphous silica-alumina support, in which process the catalyst is impregnated with an acid, followed by reduction or oxidation of the impregnated catalyst at a temperature above 200°C.

2. Process according to claim 1, wherein the precious metal is at least one of Pt, Pd, Au, Ir, Ru, Rh, Re, Os and Ag, preferably Pt and/or palladium.

3. Process according to claim 1 or 2, wherein the degree of dispersion is increased after the regeneration.

4. Process according to claims 1-3, wherein the acid impregnated catalyst is reduced in a flow of hydrogen gas.

5. Process according to claims 1-4, wherein the acid impregnated catalyst is oxidised in a flow of dry (<0.1 vol.% of water) air, followed by reduction.

6. Process according to claims 1-5, wherein the reduction and or oxidising step are carried out at a temperature of between 250 and 600°C.

7. Process according to claims 1-6, wherein the silica-alumina support has been prepared using a sol-gel method.

8. Process according to claims 1-7, wherein the support has an Si-Al atomic ratio of from 0.1 to 300.

9. Process according to claims 1-8, wherein the catalyst has a precious metal content of from 0.01 to 5 wt.%, calculated on the basis of the weight of reduced catalyst.

10. Process according to claims 1-9, wherein the catalyst is impregnated with an aqueous solution of the acid.

11. Process according to claims 1-10, wherein the acid is selected from the group of HCl, H_3PO_4, H_2SO_4, HNO_3, HBr and combinations thereof.

12. Process according to claims 1-11, wherein the amount of acid calculated on the basis of a ratio of equivalents of acid to atoms of precious metal is between 0.1 and 100, preferably between 0.5 and 10.

13. Process according to claims 1-12, wherein prior to the impregnation, carbonaceous deposits on the catalyst are burned off.

14. Process according to claim 1-13, wherein the regeneration is carried out in a reactor, separate from the reactor in which the catalyst is used.

15. Process according to claims 1-14, wherein the catalyst is a used catalyst from a process in the group consisting of hydrogenation, hydro-isomerisation, hydro-desulfurisation, hydrodewaxing and catalytic reforming.

16. Process for hydrogenation, hydro-isomerisation, hydro-desulfurisation or hydrodewaxing, comprising treating the feedstock in the presence of a catalyst that has been regenerated using the process of claims 1-15.

01/2000 FORM 11

Sheet 1 of 2
Attorney
Docket No.: VER-137XX

DECLARATION AND POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: PROCESS FOR REGENERATING A USED PRECIOUS METAL CATALYST

the specification of which (check one):

[ ] is attached hereto. [X] was filed 20-12-2000 as Application No. 09/~~172~~720,068
amended on _____ (if applicable).

[X] was filed as PCT International Application No. PCT/NL99/00389 on June 24, 1999, and was amended under PCT Article 19 on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, USC §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)		Date Filed	Priority Claimed	
98202127.1 (Number)	European Patent (Country)	25 June 1998 (Day/Month/Year)	[X] Yes	[ ] No
(Number)	(Country)	(Day/Month/Year)	[ ] Yes	[ ] No

I hereby claim the benefit under Title 35, USC §119(e) of any United States provisional application(s) listed below:

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

Express Mail Number
EL418429207US

1/2000 FORM 11 Sheet 2 of 2

Attorney
Docket No.: VER-137XX

I hereby claim the benefit under Title 35 USC §120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 USC §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business connected therewith in the Patent and Trademark Office, and to file with the USRO any International Application based thereon.

Stanley M. Schurgin, Reg. No. 20,979
Charles L. Gagnebin III, Reg. No. 25,467
Paul J. Hayes, Reg. No. 28,307
Victor B. Lebovici, Reg. No. 30,864
Eugene A. Feher, Reg. No. 33,171
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of Sole/First Inventor: Marius Vaarkamp		
City of Residence Utrecht NLX	State or Country Netherlands	Country of Citizenship Netherlands
Post Office Address Vleutenseweg 399 3532 HH Utrecht	City Utrecht	State or Country Zip Code Netherlands
Signature: (Please sign and date in permanent ink.) X		Date signed: X 19-Feb-2001

CLG:mes/240231-1